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## **JAPANESE / ENGLISH TRANSLATION OF**

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**Title: Manufacturing Method For Terephthalic Acid**

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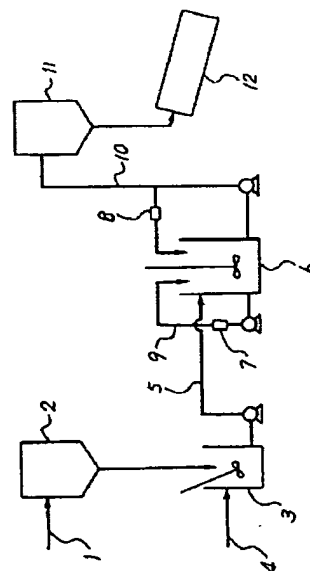
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(54) [Title of the Invention]

**Manufacturing  
Method For  
Terephthalic Acid**

(57) [Summary]

[Object] To provide a manufacturing method for terephthalic acid in which the required motive force for stirring is small when blending ethylene glycol and stirring.



**[Constitution of the Invention]** Terephthalic acid with the desired grain size distribution can be obtained as a product by means of pulverizing a terephthalic acid slurry with a wet pulverizer, measuring the grain size distribution of the pulverized terephthalic acid, and adjusting the amount of pulverizing in the wet pulverizer.

**[Claims]**

**[Claim 1]** A manufacturing method for terephthalic acid wherein a terephthalic acid slurry is fed to a solid-liquid separation means, terephthalic acid crystals and the mother liquor are separated, and the resulting terephthalic acid crystals are dried to form a terephthalic acid product, said method characterized in that at least a portion of the terephthalic acid slurry fed to the solid-liquid separation means is pulverized with a wet pulverizer, the grain size distribution of the terephthalic acid slurry that flows from the wet pulverizer or the terephthalic acid slurry being fed to the solid-liquid separation means is measured, and the pulverizing of the terephthalic acid slurry in the wet pulverizer is controlled based on the measurement results.

**[Claim 2]** A manufacturing method for terephthalic acid wherein a terephthalic acid slurry is fed to a solid-liquid separation means, terephthalic acid crystals and the mother liquor are separated, and the resulting terephthalic acid crystals are dried to form a terephthalic acid product, said method characterized in that a terephthalic acid slurry is fed to a solid-liquid separation means by way of a pulverization tank provided with a terephthalic acid grain size distribution measuring apparatus and an intermediately disposed circulation pipeline for the terephthalic acid slurry that has a wet pulverizer, the terephthalic acid slurry in the pulverization tank is circulated through the circulation pipeline while being pulverized with the wet pulverizer, the terephthalic acid slurry grain size distribution is measured with a grain size distribution measuring apparatus, and the pulverizing of the terephthalic acid slurry in the wet pulverizer is controlled based on the measurement results.

**[Claim 3]** The manufacturing method for terephthalic acid cited in claim 2, characterized in that the grain size distribution measuring apparatus for terephthalic acid slurry is disposed between the outflow of terephthalic acid slurry from the pulverization tank and the point of feeding of the terephthalic acid to the solid-liquid separator.

**[Claim 4]** The manufacturing method for terephthalic acid cited in claims 2 or 3, characterized in that the ratio of terephthalic acid circulation velocity via the circulation pipeline with respect to the terephthalic acid slurry feed velocity to the pulverization tank is 0.5 to 8.

**[Claim 5]** The manufacturing method for terephthalic acid cited in any of claims 1 to 4, characterized in that the wet pulverizer is provided with a pulverizing unit that comprises discoid fixed teeth and rotating teeth.

**[Claim 6]** The manufacturing method for terephthalic acid cited in any of claims 1 to 5, characterized in that the concentration of terephthalic acid slurry being fed to the wet pulverizer is 20 to 50 wt%.

**[Claim 7]** The manufacturing method for terephthalic acid cited in any of claims 1 to 6, characterized in that the terephthalic acid slurry fed to the wet pulverizer is obtained as a result of oxidizing *p*-xylene in an acetic acid solvent to produce terephthalic acid, recovering the resulting terephthalic acid as crystals, and reslurrying the crystals in a solvent.

**[Claim 8]** The manufacturing method for terephthalic acid cited in any of claims 1 to 6, characterized in that the terephthalic acid slurry fed to the wet pulverizer is obtained as a result of producing terephthalic acid crystals from a terephthalic acid aqueous solution, recovering the resulting terephthalic acid crystals, and reslurrying the crystals with water.

#### **[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]** The present invention relates to a method for manufacturing terephthalic acid, and more particularly to a method for manufacturing terephthalic acid with a controlled grain size distribution.

**[0002]**

**[Prior Art]** Currently, terephthalic acid is principally manufactured by way of the liquid-phase oxidation of *p*-xylene. In a typical manufacturing method, *p*-xylene and molecular oxygen-containing gas (ordinarily air) are fed to an acetic acid solvent containing manganese, cobalt, and bromine as catalysts, and *p*-xylene is oxidized to produce terephthalic acid. The solubility of terephthalic acid in an acetic acid solvent is poor, so the produced terephthalic acid is precipitated and is present in the form of a terephthalic acid slurry. Normally, the terephthalic

acid in the terephthalic acid slurry contains a large quantity of impurities, and further refinement is needed. In one typical refinement method, the terephthalic acid slurry is further finely oxidized with molecular oxygen-containing gas at an even higher temperature to form a high-purity terephthalic acid, and the solid and liquid are then separated and dried to obtain a terephthalic acid product. In another typical manufacturing method, the terephthalic acid crystals are separated from the terephthalic acid slurry that has been discharged from the oxidation reaction system, the crystals are dissolved in water under high temperature and pressure to form an aqueous solution, and the resulting solution is passed together with hydrogen gas through a noble metal catalyst bed. It is thought that the impurities in the terephthalic acid are thereby changed into a form that is easily dissolved in water. The aqueous solution that has passed through the noble metal catalyst bed is cooled to precipitate terephthalic acid, is subjected to solid-liquid separation, and is dried to form a terephthalic acid product. Terephthalic acid is principally reacted with ethylene glycol and used as polyethylene terephthalate to manufacture synthetic fibers, films, bottles, and other products.

**[0003]**

**[Problems to Be Solved by the Invention]** Reacting terephthalic acid with ethylene glycol entails reacting solid terephthalic acid suspended in a slurried state in liquid ethylene glycol, so a considerable amount of motive force is required in the stirring step. A need therefore exists for terephthalic acid in which a minimal amount of motive force is required for stirring.

**[0004]** The motive force required for stirring depends on the grain size distribution of the terephthalic acid, and the motive force required for stirring can be kept to a constant minimal value by way of controlling the grain size distribution. In the above-described methods for manufacturing terephthalic acid, however, it is very difficult to control conditions during terephthalic acid precipitation to obtain a desired grain size distribution. One reason is the narrow range in which the conditions during terephthalic acid precipitation can be manipulated. Another reason is that the required time until the product is obtained from terephthalic acid precipitation is long, and a large quantity of terephthalic acid is present during this interval, so the time delay until the effect of modifying the precipitation conditions is manifest in the product is considerable, and the effects are not apparent in some cases. An object of the present

invention is to therefore provide a manufacturing method for terephthalic acid in which the desired grain size distribution of terephthalic acid can easily be obtained.

[0005]

**[Means Used to Solve the Above-Mentioned Problems]** In accordance with the present invention, terephthalic acid having a desired grain size distribution can be easily manufactured using manufacturing method for terephthalic acid wherein a terephthalic acid slurry is fed to a solid-liquid separation device, terephthalic acid crystals and the mother liquor are separated, and the resulting terephthalic acid crystals are dried to form a terephthalic acid product, the method characterized in that at least a portion of the terephthalic acid slurry fed to the solid-liquid separation device is pulverized with a wet pulverizer, the grain size distribution of the terephthalic acid slurry that flows from the wet pulverizer or the terephthalic acid slurry being fed to the solid-liquid separation device is measured, and the pulverizing of the terephthalic acid slurry in the wet pulverizer is controlled based on the measurement results.

[0006]

**[Embodiments of the Present Invention]** The detailed description of the present invention will show that, rather than controlling the conditions for producing terephthalic acid crystals, the present invention attempts to acquire terephthalic acid crystals having the desired grain size distribution as a result of pulverizing the produced terephthalic acid in a slurried state. In accordance with the research of the present inventors and others, both the terephthalic acid crystals produced in the *p*-xylene oxidation reaction, and the terephthalic acid crystals produced with a stepwise temperature reduction of the terephthalic acid aqueous solution ordinarily have a relatively large grain size. Pulverizing the crystals easily changes these to a grain size distribution in which the required motive force for stirring is smaller when the crystals are mixed with ethylene glycol and formed into a slurry.

[0007] The terephthalic acid slurry provided to the pulverization step can be one that is produced as a result of oxidizing *p*-xylene in an acetic acid solvent and is additionally oxidized for further refinement. As another method, it is also possible to use terephthalic acid crystals that are obtained by means of subjecting the terephthalic acid slurry produced as a result of oxidizing *p*-xylene in an acetic acid solvent to solid-liquid separation, and reslurrying with a new solvent.

Also may be used, for example, is one which the terephthalic acid slurry described above is subjected to solid-liquid separation in a decanter or the like, and water, acetic acid, or another new solvent is added to the separated terephthalic acid crystals to reslurry the crystals. In this case, reslurrying is preferably performed with a hot solvent at a temperature of 80 to 100°C in order to enhance the washing effect on the crystals. In other words, when the method for reslurrying with the aid of the new solvent is used, the concentration of the terephthalic acid slurry can be adjusted to any favorable concentration in the wet pulverizer, and the method also has the added benefit of washing the terephthalic acid crystals. A strong mechanical force operates on the terephthalic acid crystals during wet pulverizing, so impurities adhering to the surface are easily removed. The impurities contained therein are exposed on the surface and eluted in the solvent as a result of pulverizing the terephthalic acid crystals. A thorough washing effect is obtained when the concentration of impurities in the solvent is low, and the adherence of impurities to the new surfaces created by the pulverizing is minimal. Yet another method recovers terephthalic acid crystals from the terephthalic acid slurry produced as a result of oxidizing *p*-xylene, and dissolves the crystals in water under a high temperature and pressure. This aqueous solution is passed together with hydrogen through a noble metal catalyst bed and refined, and the resulting solution is cooled and once again formed into a terephthalic acid slurry. It is also possible to use a product in which these terephthalic acid crystals are recovered and reslurried with water.

[0008] A high-speed rotary or high-speed agitating wet pulverizer is ordinarily used. A pulverizer that grinds is preferred over a pulverizer that crushes the terephthalic acid grains. When such a pulverizer is used, the surfaces of the coarse grains are cut away to produce a smaller grain diameter, resulting in a rounded shape. The amount of fine powder increases at the same time, and this improves the slurry characteristics and the fluidity and reaction of the fine particles. Because of its use in the present invention, a high-speed rotary wet pulverizer provided with a fine particle unit comprising discoid fixed teeth and rotating teeth is particularly advantageous. In this type of pulverizer, a plurality of blades or grooves are provided respectively to the fixed teeth in concentric circles from the center portion thereof, and to the rotating teeth radially from the center of the axis of rotation.

[0009] The energy required for pulverizing is ordinarily 0.5 to 10 kWh per 1 m<sup>3</sup> of terephthalic acid slurry, and the amount of pulverizing can be controlled by means of adjusting the

pulverization energy to be applied. The pulverization energy can be easily varied by way of varying the rotational speed, but it is also possible to vary the energy by means of varying the gap and the type of fixed and rotating teeth in the high-speed wet pulverizer. The concentration of terephthalic acid slurry fed to the pulverizer is ordinarily 10 to 60 wt%, and is preferably 20 to 50 wt%.

[0010] The pulverizer can be disposed directly in an intermediate position in the pipeline that feeds the terephthalic acid slurry to the solid-liquid separation device, but the pulverization tank provided with a slurry circulation pipeline is preferably disposed in an intermediate position in the pipeline, and the pulverizer is preferably disposed in the slurry circulation pipeline. Such a configuration allows the ratio (B/A) of the circulation velocity (B, m<sup>3</sup>/hr) of the terephthalic acid slurry that flows through the slurry circulation pipeline with respect to the supply velocity (A, m<sup>3</sup>/hr) of the terephthalic acid slurry to the pulverization tank, in other words, the grain size distribution of the terephthalic acid slurry, to be kept to the desired value by means of adjusting the circulation ratio. The circulation ratio is normally 0.5 to 8. If the ratio is less than 0.5, it is often difficult to achieve the desired grain size distribution. A ratio that is greater than 8 is disadvantageous in that a large-capacity pulverizer is required, and the required motive force is excessive. An advantageous circulation ratio is commonly 0.8 to 4.

[0011] The grain size distribution of the terephthalic acid slurry that has been pulverized in the present invention is measured, and the amount of pulverizing is adjusted so as to obtain the desired grain size distribution. The measurement of the grain size distribution can be performed at any location between the pulverization point and the point of feeding the terephthalic acid slurry to the solid-liquid separation device. Normally, the measurement is preferably performed when feeding the terephthalic acid slurry to the solid-liquid separation device. However, when the above-described pulverization tank is provided and pulverization is conducted at a high circulation ratio, measurement may also be carried out in the circulation pipeline between the discharge port of the wet pulverizer, in other words, the point at which the terephthalic acid slurry flows from the wet pulverizer, and the point at which the terephthalic acid flows into the pulverization tank.

[0012] The measurement of the grain size distribution may be conducted with the laser diffraction/scattering method, precipitation optical transmission method, electrical resistance method, microscope method, sieving method, or other direct method in addition to a viscometer



or other indirect method. Preferably used is an automatic analyzer that uses the laser diffraction/scattering method and is capable of continuous measurement. In other words, the analyzer is disposed in the pipeline for feeding terephthalic acid slurry to the solid-liquid separation device, and the circulation ratio and the rotational speed of the pulverizer in the pulverization tank should be varied in accordance with the difference between the measured grain size distribution and the desired grain size distribution.

[0013] An example of an embodiment of the present invention will now be described with reference to the diagram. The terephthalic acid slurry to be fed from the oxidation reactor or the crystallization tank by way of a conduit 1 is separated into terephthalic acid crystals and mother liquor in a solid-liquid separator 2. The terephthalic acid crystals are fed to a slurring tank 3, and formed into a terephthalic acid slurry with a concentration of 20 to 50 wt% in water, acetic acid, or another solvent fed from a conduit 4. This slurry is fed to a pulverization tank 6 by way of a conduit 5. A circulation pipeline 9 with a high-speed wet pulverizer 7 disposed therein is provided to the pulverization tank 6, and the terephthalic acid slurry is circulated one to three times through the circulation pipeline so as to be pulverized. The terephthalic acid slurry that has achieved the desired grain size distribution is discharged from the pulverization tank through a conduit 10, and fed to a centrifugal separator, a suction filter, or another solid-liquid separator 11; a branch pipe to the pulverization tank is provided to an intermediate position thereof; a grain size distribution meter 8 is disposed in this branch pipe to continuously measure the grain size distribution of the terephthalic acid slurry; and the rotational speed and circulation ratio of the pulverizer is adjusted based on the results thereof. The terephthalic acid crystals discharged from the solid-liquid separator 11 are dried in the drier 12, yielding the product.

[0014]

**[Working Examples]** The present invention is subsequently described in greater detail with working examples; however, the working examples below do not impose any limitation on the present invention as long as the scope thereof is not exceeded. In the tables containing the results, the term "slurry torque" is defined as the agitation torque (gcm) developed when terephthalic acid and ethylene glycol are mixed in a 1:1.1 molar ratio and agitated with a double wing paddle agitator. The term "fine particle discharge time" is defined as the time (seconds) required to discharge 300 g of terephthalic acid from a cylindrical hopper with an aperture of

64 mm<sup>2</sup>, and is the flow property index. Also, "grain size distribution" is measured using an inline laser diffraction/scattering grain size distribution measuring apparatus (LASENTEC M300).

[0015] (**Working Example 1**) A 40 wt% acetic acid slurry of crude terephthalic acid obtained as a result of liquid-phase oxidizing *p*-xylene with molecular oxygen in the presence of a catalyst containing cobalt, manganese, and a bromine compound in an acetic acid solvent was additionally oxidized for further refinement under a higher temperature than the reaction temperature, and then cooled to 102°C in a stepwise fashion in a crystallization tank provided with an inline three-stage agitator. This slurry was continuously fed to a pulverization tank at a velocity of 39 m<sup>3</sup> per hour, and the liquid amount in the pulverization tank was kept at 6.0 m<sup>3</sup> as the slurry was continuously discharged.

[0016] A circulation pipeline having a wet pulverizer with high-speed rotating blades (the diameters of the fixed teeth and rotating teeth were respectively 46 cm) was provided at an intermediate position in the pulverization tank, and the circulation and pulverization treatment was performed. The gap between the fixed teeth and the rotating teeth was 1.0 mm, and the amount of slurry circulated in the pulverizer was set to 61 m<sup>3</sup>/h.

[0017] A laser diffraction/scattering grain size distribution measuring apparatus was disposed in the pipeline from the pulverization tank to the centrifugal separator, the grain size distribution was constantly monitored, and the rotational speed of the rotating teeth of the wet pulverizer was adjusted so that the grain size distribution was kept at a target level. When a stable state was achieved, the rotational speed of the wet pulverizer was set to 2,070 rpm, and the pulverization energy applied per 1 m<sup>3</sup> of the terephthalic acid slurry that was continuously discharged from the pulverization tank was 4.1 kWh.

[0018] The terephthalic acid slurry discharged from the pulverization tank was formed into a product by way of the centrifugal separator, acetic acid washing tank, suction filter, and drier. The grain size distributions of the terephthalic acid slurry that flowed from the pulverization tank and the terephthalic acid slurry fed to the pulverization tank in a stable state are noted in Table 1. The slurry torques and fine particle discharge times of the terephthalic acid product and the terephthalic acid obtained as a result of subjecting the terephthalic acid slurry fed to the pulverization tank to solid-liquid separation are listed together in Table 1.

[0019]

[Table 1]

		Slurry fed to pulverization tank	Slurry flowing from pulverization tank
Grain size distribution wt%	213 microns <	4.4	3.6
	180 to 213	7.8	7.1
	151 to 180	10.6	9.8
	108 to 151	22.8	21.5
	77 to 108	19.9	19.4
	46 to 77	23.8	24.3
	46 microns >	10.7	14.3
Average grain diameter ( $\mu\text{m}$ )		100	94
Slurry torque (gcm)		580	270
Fine particle discharge time (seconds)		11.3	15.0

[0020] (Working Example 2) Crude terephthalic acid obtained as a result of oxidizing *p*-xylene was dissolved in water under high temperature and pressure to form an aqueous solution. The solution was passed together with hydrogen through a noble method catalyst bed for further refinement. The first stage was then set to 248°C in the crystallization tank that was provided with an inline five-stage agitator, the second stage was set to 200°C, the remaining stages were successively cooled in a stepwise fashion, with stage five set to 152°C, and the terephthalic acid was crystallized. The terephthalic acid in the slurry was subjected to centrifugal separation, a slurry with 40 wt% water was formed with hot water at 98°C, and the slurry was continuously fed to the same pulverization tank as the one used in working example 1 at a velocity of 40 m<sup>3</sup> per hour.

[0021] Other than setting the gap between the fixed teeth and the rotating teeth to 1.5 mm, the pulverizing action was carried out in the same manner as described in Working Example 1. When a stable state was achieved, the rotational speed of the wet pulverizer was set to 1,900 rpm, and the pulverization energy applied per 1 m<sup>3</sup> of terephthalic acid slurry that was continuously discharged from the pulverization tank was 3.0 kWh. The results are shown in Table 2.

[0022]

[Table 2]

		Slurry fed to pulverization tank	Slurry flowing from pulverization tank
Grain size distribution wt%	213 microns <	15.5	9.7
	180 to 213	10.5	9.7
	151 to 180	12.4	12.1
	108 to 151	21.4	21.5
	77 to 108	14.2	13.9
	46 to 77	16.0	16.5
	46 microns >	10.0	16.6
Average grain diameter ( $\mu\text{m}$ )		129	115
Slurry torque (gcm)		340	160
Fine particle discharge time (seconds)		7.3	11.2

**[Brief Description of the Drawings]**

[Figure 1] A diagram schematically showing an example of the apparatus for implementing the present invention.

**[Key]**

- 1: Terephthalic acid slurry supply tube
- 2: Solid-liquid separator
- 3: Slurry formation tank
- 4: Solvent supply tube
- 5: Terephthalic acid slurry conduit
- 6: Pulverization tank
- 7: Wet pulverizer
- 8: Grain size distribution meter
- 9: Circulation pipeline
- 10: Slurry conduit
- 11: Solid-liquid separator
- 12: Drier

Fig. 1

